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The fate of silver nanoparticles in soil solution — Sorption of solutes and aggregation

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HIGHLIGHTS

- Soil solution reduces the release of ionic silver from Ag NP.
- The stabilizing effect of sorbed organic matter is dependent on Ag NP concentration.
- Short-chained DOM is preferentially adsorbed over long-chained, aromatic DOM.
- Ag NP may form a sink for Ag^+ ions in the soil.

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ABSTRACT

Nanoparticles enter soils through various pathways. In the soil, they undergo various interactions with the solution and the solid phase. We tested the following hypotheses using batch experiments: i) the colloidal stability of Ag NP increases through sorption of soil-borne dissolved organic matter (DOM) and thus inhibits aggregation; ii) the presence of DOM suppresses Ag oxidation; iii) the surface charge of Ag NP governs sorption onto soil particles. Citrate-stabilized and bare Ag NPs were equilibrated with (colloid-free) soil solution extracted from a floodplain soil for 24 h. Nanoparticles were removed through centrifugation. Concentrations of free Ag ions and DOC, the specific UV absorbance at a wavelength of 254 nm, and the absorption ratio $\alpha_{254}/\alpha_{410}$ were determined in the supernatant. Nanoparticle aggregation was studied using time-resolved dynamic light scattering (DLS) measurement following the addition of soil solution and 1.5 mM Ca^{2+} solution. To study the effect of surface charge on the adsorption of Ag NP onto soil particles, bare and citrate-stabilized Ag NP, differing in the zeta potential, were equilibrated with silt at a solid-to-solution ratio of 1:10 and an initial Ag concentration range of 30 to 320 μg/L. Results showed that bare Ag NPs sorb organic matter, with short-chained organic matter being preferentially adsorbed over long-chained, aromatic organic matter. Stabilizing effects of organic matter only come into play at higher Ag NP concentrations. Soil solution inhibits the release of Ag^+ ions, presumably due to organic matter coatings. Sorption to silt particles was very similar for the two particle types, suggesting that the surface charge does not control Ag NP sorption. Besides, sorption was much lower than in comparable studies with sand and glass surfaces.

1. Introduction

Engineered inorganic nanoparticles (EINPs) can enter soils through various sources and pathways such as the application of fertilizers and plant protection products (Batley et al., 2013), biosolids (Benn and Westerhoff, 2008), the irrigation of sewage water (Gottschalk et al., 2009) or the flooding of floodplains (Lecoanet et al., 2004). According to a material flow analysis from a life-cycle perspective of EINP-containing products, an increasing soil exposure to Ag NP has to be expected (Gottschalk et al., 2009). Silver NPs are considered to have a

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cumulative impact on environmental and human health (Anjum et al., 2013).

Once nanoparticles (NPs) have entered the soil, they are subject to reactions with the soil solution as well as with the (mobile and stationary) solid phase. Nanoparticle stability in soils is affected by various processes and environmental factors. With the study presented here we address Ag NP (1) and their coating by dissolved organic matter (DOM), (2) their dissolution and (3) their sorption to soil particles. Thereby our study represents one of the first screenings of important soil processes and an assessment of their relevance for the fate of nanoparticles determined through the use of a natural soil extract.

Coating by dissolved organic matter. The coverage through dissolved organic matter is reported to influence NP stability (Lecoanet et al., 2004). Several authors found an increase in Ag NP stability through the sorption of fulvic and humic acids (Li et al., 2010) as well as Suwannee River Humic Acid (Huynh and Chen, 2011). However, to the best of our knowledge, the sorption of soil-borne dissolved organic matter to Ag NP has so far not been investigated. The presence of divalent cations is known to decrease the stability of pedogenic colloids as well as of NP as they screen the surface charge of particles, thus facilitating aggregation (Klitzke and Lang, 2009; Klitzke et al., 2012; Li et al., 2010). Despite these two counteracting processes, i.e. stabilization through dissolved organic matter sorption and cation-induced aggregation, it is widely assumed that reactions occurring in soils might increase NP stability and thus enhance NP mobility (Darlington et al., 2009; Nel et al., 2006).

Dissolution. The dissolution of NP may release toxic compounds into the environment (Batley et al., 2013). The release of Ag^+ from Ag NP has been observed in different sample matrices, e.g. in well-defined aqueous media with varying pH, concentrations of natural organic matter (NOM) and ocean salts (Liu and Hurt, 2010) as well as in artificial soil solution (Cornelis et al., 2012). On the basis of the results by Liu and Hurt (2010), who found Ag^+ release to be highest at low pH (ie. pH 4) and in the absence of NOM, one may presume Ag NP oxidation in neutral soil solutions to play only a minor role. Oxidized Ag ions may sorb to Ag NP surfaces (Liu and Hurt, 2010), from where they may diffuse away from NP surface into the bulk solution (Borm et al., 2006). While NOM was reported to inhibit Ag NP oxidation (Liu and Hurt, 2010), the presence of cations would promote Ag oxidation as it may displace Ag^+) ions from the particle surface, thus enhance oxidation (Li et al., 2010). So far, it is unclear, to which extent Ag^+ ions oxidized by components of the soil solution are released into the bulk solution, i.e. which fraction remains adsorbed on NP surface as an exchangeable ion with the NP surface acting as a sink of Ag^+ ions.

Sorption to soil particles. The surface charge is considered to be an important parameter governing heteroaggregation (Cornelis et al., 2013) and sorption to silica surfaces is supposed to decrease with increasing negative particle charge (Thio et al., 2012).

The aim of this work was to assess the impact of the soil solution of a flood plain soil on the fate and stability of Ag NP as well as the interaction of Ag NP with natural soil particles by testing the following hypotheses:

i) Colloidal stability of Ag NP increases through the sorption of soil-borne dissolved organic matter and thus inhibits aggregation.
ii) The presence of soil-borne DOM suppresses Ag oxidation and thus reduces the amount of exchangeable Ag^+ adsorbed on Ag NP surfaces.
iii) The surface charge of Ag NP governs sorption onto soil particles, i.e. bare Ag NP show higher sorption to soil particles than Ag NP which are stabilized through additional charges.

These hypotheses were tested with batch experiments.

2. Material and methods

2.1. Preparation of silver nanoparticle suspensions

Citrate-coated Ag NPs were prepared according to the following procedure: Synthesis of Ag NP was performed using Turkevich method (Turkevich et al., 1951) which was modified for Ag. One millimole silver nitrate ($AgNO_3$, ≥99.9%, p.a., Roth) and 5 mmol trisodium citrate ($Na_3C_6H_5O_7$, Sigma-Aldrich) were dissolved in 50 mL and 950 mL demineralised water (18.2 MΩ cm, Direct-Q UV, Millipore) respectively. In the solution of trisodium citrate the pH value was adjusted to 11 using 1 mol/L sodium hydroxide solution (NaOH, 1 N standard solution, Roth). Solution of trisodium citrate was heated to boiling in a covered beaker glass under magnetic stirring (RCT basic, IKA Labortechnik). After the boiling started 50 mL silver nitrate solution was added dropwise to the trisodium citrate solution within 4.5 min. The colour of the reaction solution changed from transparent-colourless to yellow and later to greyish-turbid. The reaction solution was then boiled for 20 min. After this period the solution was cooled to room temperature. The prepared silver nanoparticle stock dispersion was kept at +4 °C in the dark for further use.

Particle size distribution and mean particle diameter (z-average) were determined using dynamic light scattering instrument (Delsa Nano C Particle Analyser, Beckman Coulter). Particle size was measured before and after dilution of silver nanoparticle stock dispersion. For dilution, 1 mL stock dispersion was mixed with 2 mL demineralised water directly in the measuring cuvette. Mean hydrodynamic particle diameters (z-average) measured in undiluted and diluted stock dispersions were 31.2 ± 1.2 nm.

To determine dissolved silver concentration in the stock dispersion, nanoparticles were first separated from the liquid phase, and then the Ag concentration was measured in the liquid phase. Dissolved Ag is defined in this work as a fraction with a diameter of <2 nm. To reach this cut-off, the separation of silver nanoparticles from the liquid phase was performed using ultracentrifuge (SORVALL WX 90 Ultra, Thermo Electron Corporation). Silver NP stock dispersion (distributed in two 8.5 mL ultracentrifuge tubes) was centrifuged at 80,000 rpm (396,000 g) for 2 h (acceleration time from 0 to 500 rpm: 6 min and from 500 to 80,000 rpm: approx. 4 min; deceleration time from 80,000 to 500 rpm: approx. 4 min and 500 to 0 rpm: 6 min). After centrifugation, 5 mL of supernatant was removed carefully from each tube, mixed together, and stabilised with 1% nitric acid (sub-boiled). The samples were prepared in triplicate. Stabilised samples were analysed using inductively coupled plasma mass spectrometer (ICP-MS, XSeries 2, Thermo Scientifc). Mean concentration of dissolved Ag (<2 nm) in the Ag nanoparticle stock dispersion was 54 ± 26 μg/L (standard deviation).

Bare Ag NPs with a primary particle size (as indicated by the manufacturer) of 35 nm were obtained from Iolitec nanomaterials. For the DOM sorption experiment, dispersions were prepared in duplicate by weighing 40 mg Ag NP in 40 mL Millipore water. The mixtures were sonicated with an ultrasonic finger at 5400 W/mL for 35 min each and subsequently filtered over a 0.2 μm polyether sulfone membrane (Pall). Both suspensions were joined together. The final concentration of Ag NP amounted to 153 μg/L. The measured (intensity-based) particle diameter by dynamic light scattering (HPPS — High Performance Particle Sizer, Malvern Instruments) was 39.5 ± 8.5 nm. Further NP characteristics have been reported by Abraham et al. (2013). To achieve different initial concentrations for the sorption experiment onto silt, the amount of weighed Ag NPs and the volume of Millipore water were varied.

Table 1
Composition of the soil solution used for the ageing experiments. n. d.: not detected.

Concentrations [mg/L]	
Ca	61.0 ± 0.4
Fe	0.0 ± 0.0
K	2.2 ± 0.0
Mg	6.6 ± 0.1
Mn	0.0 ± 0.0
P	0.2 ± 0.0
Al	n. d.
Na	6.2 ± 0.9
Cl^-	10.2 ± 0.0
NO_3^-	28.9 ± 0.0
SO_4^{2-}	8.3 ± 0.0
DOC	21.0 ± 0.9

2.2. Soil samples and soil solution

Soil samples were taken from the floodplain area of the River Rhine (stagnic Fluvisol) near Karlsruhe (Germany) and classified as silty clay (organic carbon content 6.2%; C/N-ratio 21.5). The site was chosen as the aquatic–terrestrial interface in floodplain soils is of particular relevance: NP which entered streams through wastewater treatment plants may access groundwater and riverbank filtrate, thus posing a potential risk for these environmental compartments.

The soil material was sieved to 2 mm and stored field-moist in the refrigerator following sampling. Soil solution was obtained by equilibrating field-moist soil in a solid–solution-ratio of 1:2.5 on an end-over-end shaker (20 rpm; GFL 3040) for 16 h and subsequent filtration over a 1.2 μm cellulose-nitrate membrane (Sartorius, Type 11303–047 N). To obtain a soil solution free of soil-borne colloids, the suspension was ultracentrifuged (Beckman Optima TL) at 132,750 × *g* for 4 h to remove any colloidal material larger than a diameter of 16 nm (assuming a density of 1.2 g/cm^3).

Concentrations of organic carbon, Na, K, Ca, Mg, Mn, Al, Fe, and P were determined in triplicate samples in the supernatant by a TOC analyser (TOC — 5050 A Shimadzu) and ICP-OES (iCAP 6000, Thermo Scientific) following acidification with dilute HCl (for DOC analysis) and dilute HNO_3 (for inorganic elements), respectively. Concentrations of chloride, nitrate, and sulphate were determined using ion chromatography (DIONEX, DX-120, see Table 1).

Soil samples from the A_l-horizon of a Luvisol in Bad Gandersheim (Germany) were taken and classified as strongly clayey silt: Clay and silt fractions were separated from each other through repeated cycles of suspending the soil in water and subsequent sedimentation of the silt fraction. The clay fraction remained suspended in the water, which was then removed. The settled silt was air-dried and used for sorption studies with Ag NP. Its organic carbon content was 0.23% and C/N-ratio 8.1. X-ray fluorescence analysis (PW2400, Philips) of the dried silt (105 °C) revealed a composition of 85.3% SiO_2, 6.4% Al_2O_3, 1.3% Fe_2O_3, 2.2% K_2O and 0.9% Na_2O.

2.3. Experiments and analyses

2.3.1. Batch experiments to determine Ag^+ release

To determine the release of Ag^+ ions, citrate-stabilized Ag NPs were mixed with (i) soil solution extracted from the floodplain soil and (ii) Millipore water to obtain a final Ag NP concentration of 4 mg/L. Both types of samples were set up in triplicate. They were equilibrated for 24 h on an end-over-end shaker (20 rpm, GFL 3040) and subsequently centrifuged for 45 min at 30000 rpm (i.e. 47,790 × *g*) to remove Ag NP larger than 4.4 nm in radius. An aliquot of the supernatant was acidified with diluted nitric acid for the determination of dissolved Ag through ICP-OES-analysis.

To determine exchangeable Ag^+ ions sorbed on the NP surface, 18 mL of the uncentrifuged sample were mixed with 2 mL 1 M NH_4NO_3 in plastic containers and shaken for 2 h on an end-over-end shaker (20 rpm) prior to centrifugation (for details see above). An aliquot of the supernatant was acidified with dilute nitric acid for subsequent determination of Ag by ICP-OES analysis.

2.3.2. Batch experiments to determine sorption of dissolved organic matter from soil solution

The soil solution prepared as previously described was used pure (100%) as well as diluted with Millipore water (0%, (i.e. Millipore water); 25, 50, and 75%) to obtain different levels of DOM. Three parts of soil solution were mixed with 1 part of a suspension of bare Ag NP (for preparation see above) in glass containers, yielding a final Ag NP concentration of 38 μg/L. The pH of the mixtures amounted to 7.8 ± 0.2. Samples were equilibrated for 24 h on a horizontal shaker (130 rpm; KS501 digital, IKA Labortechnik). Afterwards, samples were centrifuged for 15 min at 7646 × *g* to remove Ag NP from suspension. In the supernatant, DOC concentrations were determined with a TOC analyser as well as the optical density at λ = 254 and 410 nm with a UV/VIS spectrometer (Lambda 20, Perkin Elmer).

For the supernatant, the specific UV absorbance ($SUVA_{254}$) as well as the absorption ratio $\alpha_{254}/\alpha_{410}$ (Spencer et al., 2007) were calculated. The $SUVA_{254}$ value [m ∗ L/mg] is defined as the absorbance at a wavelength of λ = 254 [m] divided by the DOC concentration [mg/L] of a solution. It is a measure for the aromaticity of a dissolved organic matter solution (Weishaar et al., 2003). It increases with increasing aromaticity. The ratio $\alpha_{254}/\alpha_{410}$ is considered a proxy for molecular weight (Spencer et al., 2007).

2.3.3. Nanoparticle characteristics

To determine the impact of soil solution on the zeta potential as well as the particle size, citrate-stabilized Ag NP were equilibrated with the soil solution at a Ag NP concentration of 5 mg/L and pH of 7.8 ± 0.1 on a horizontal shaker (130 rpm; KS501 digital, IKA Labortechnik) for 24 h. Blank samples prepared with Millipore water instead of soil solution were set up in the same way. Zeta potential was calculated based on the electrophoretic mobility of the nanoparticles using the Helmholtz–Smoluchowski equation, which was analysed by a Zetasizer 2000 photon (Malvern Instruments). Particle size and particle topography were determined by scanning electron microscopy (Hitachi S-2700) coupled with an energy-dispersive analysis of X-rays (EDX; EDAX, software 'TEAM', detector 'Apollo' — acquisition parameters of the beam: accelerating voltage: 15 kV, beam current: 0.1 nA). The suspensions were applied onto a silicon wafer and air-dried.

2.3.3.1. Point of zero charge. To study the impact of the soil solution on the point of zero charge of Ag NP samples equilibrated in soil solution and Millipore water were prepared as described above. To delineate the impact of Ca^{2+} in the soil solution, an additional Ag NP suspension (c(AgNP) = 5 mg/L) was prepared correspondingly, to which appropriate amounts of a 15 mM $Ca(NO_3)_2 * 4H_2O$ solution were added to yield a final Ca^{2+} concentration of 1.5 mM, which corresponds to the Ca^{2+} concentration in the soil solution. The pH (1–8) of these samples was adjusted through the addition of dilute nitric acid or a dilute solution of KOH for subsequent zeta potential measurement.

2.3.3.2. Aggregation kinetics. To study the impact of soil solution on Ag NP stability and to delineate the role of the Ca^{2+} ion, the aggregation kinetics of citrate-stabilized Ag NP was determined by adding i) soil solution (1.5 mmol/L Ca^{2+}, 16 mg/L DOC) and ii) Ca^{2+} solution

($Ca(NO_3)_2 * 4H_2O$; 15 mmol/L Ca^{2+}) to Ag NP, yielding final Ca^{2+} concentrations of 1.5 mmol/L and 9 mmol/L in the sample. To study the impact of varying initial Ag NP concentrations, these were adjusted to 0.5, 5 and 10 mg/L Ag. The respective solutions were thoroughly mixed with particle suspensions in a beaker prior to time-resolved determination of particle size during a period of 1 1/2 h using dynamic light scattering measurements (HPPS — High Performance Particle Size, Malvern Instruments). An empirical model was fitted to the data (Eq. (1)) in order to parameterize the maximum particle diameter and the rate constant,

$$d(t) = (d_\infty - d_{init})\,(1 - e^{-kt}) + d_{init} \quad (1)$$

with t [h] being time, d [nm] the particle diameter as a function of time, d_∞ [nm] the particle diameter at $t = \infty$, d_{init} [nm] the initial particle diameter, and k [1/h] being the rate constant, which is associated with the reaction rate. The parameters k and d_∞ are the parameters which are estimated by a non-linear least-squares regression.

2.3.4. Sorption of Ag NP to silt grains

Silt was dispersed in a soil-to-solution ratio of 1:10. The pH was adjusted to 6.5 using dilute KOH solution and the ionic strength set to 3 mmol/L using dilute KNO_3 solution. Initial concentrations (c0) of bare and citrate-stabilized Ag NP were adjusted to a range from 30 to 320 μg/L. Triplicate samples were prepared per adjusted concentration. The samples were shaken for 24 h on an end-over-end shaker (20 rpm; GFL 3040) prior to filtration over a 1.2 μm cellulose-acetate membrane (Sartorius, type 12303-047-K). Silver NP concentrations in the filtrate were determined by ICP-OES (iCAP 6000, Thermo Scientific) following 24 h digestion in 5% nitric acid. Differences between c0 and Ag concentrations in the filtrate correspond to the amount of Ag sorbed to silt grains.

3. Results and discussion

3.1. Sorption of organic matter to Ag NP and the effect of soil solution on Ag NP stability

3.1.1. Sorption of organic matter to Ag NP

The results show that bare Ag NPs sorb organic matter (Fig. 1). The $SUVA_{254}$ value in the supernatant increases following DOM sorption (Fig. 2), suggesting that non-aromatic compounds were preferentially removed from solution through sorption to Ag NP. The $\alpha_{254}/\alpha_{410}$-ratio increases when high molecular weight (HMW) organic matter is preferentially retrieved from solution. Our data suggest that this ratio is concentration-dependent (Fig. 3). At high DOM concentration, the decreasing ratio suggests the preferential sorption of low molecular weight (LMW) organic matter. Summing up, this experiment indicates

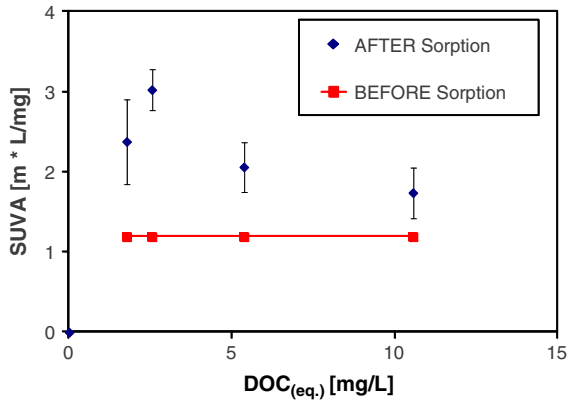

Fig. 2. Specific UV-absorbance (SUVA) of the solution as a function of DOC equilibrium concentration before and after sorption to Ag NP.

that short-chained, non-aromatic organic matter is preferentially adsorbed onto the Ag NP over long-chained aromatic DOM. These results are contrary to findings from other studies which report preferential adsorption of high molecular weight organic matter onto Fe-oxide nanoparticles (Chekli et al., 2013) and onto multi-walled carbon nanotubes (Hyung and Kim, 2008). This discrepancy might be ascribed to the presence of divalent cations in our soil solution, which are known to enlarge organic molecules (Kunhi Mouvenchery et al., 2012) through cross-linking and thereby facilitating sorption to NP surface. Sánchez-Cortés et al. (1998) investigated the sorption of organic matter extracted from a peat soil to Ag NP. At neutral pH, they found high molecular weight humic acids and low molecular weight fulvic acids to strongly attach to the particle surface. Divalent cations could facilitate the sorption of low molecular weight organic matter like these fulvic acids, which would have the consequence that divalent cations play a key role in the sorption of organic matter to Ag NP. As the size of the sorbing organic matter may have a strong effect on NP stability (Louie et al., 2013) an understanding of the mechanisms governing DOM sorption to NP is crucial and thus merits further research.

3.1.2. Zeta potential of Ag NP

Incubation of Ag NP in soil solution resulted in a decrease in the absolute value of the zeta potential, i.e. from −59 mV to −15 mV, suggesting a decrease in Ag NP stability. Exposure of Ag NP to soil solution also lowers the isoelectric point by more than 1 pH unit (Fig. 4). We attribute this to the sorption of soil-borne organic matter, which presumably has a higher acidity than citric acid. Furthermore, the course of the curve of the soil-aged Ag NP is flatter than the one of the original Ag NP and coincides with the curve of the Ca^{2+} solution

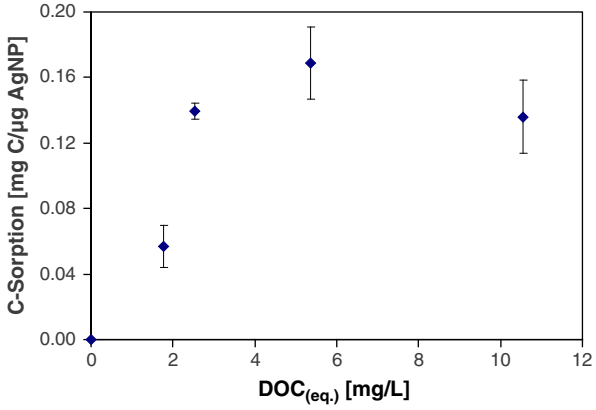

Fig. 1. Sorption of organic matter to bare Ag NP as a function of DOC equilibrium concentration.

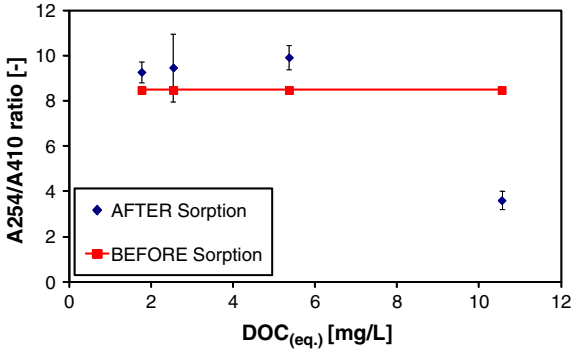

Fig. 3. α254/α410 ratio of the solution as a function of DOC equilibrium concentration before and after sorption to Ag NP.

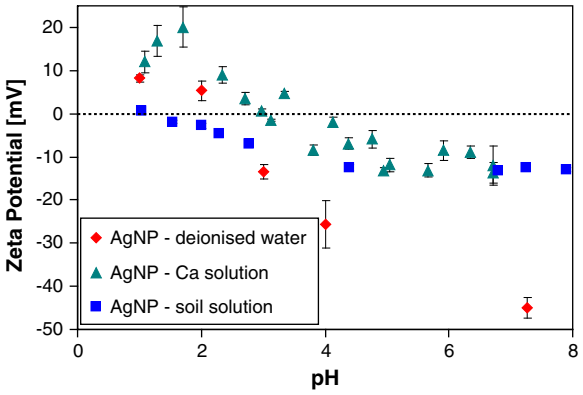

Fig. 4. Zetapotential of citrate-stabilized Ag NP as a function of pH following equilibration in Millipore water, soil solution and Ca^{2+} solution.

above the point of zero charge. This flatter course may be explained with the effect of Ca^{2+}, shielding the negative charges (Philippe and Schaumann, 2014). This decrease in Ag NP stability in soil solution goes along with a dramatic increase in Ag NP size leading to Ag NP clusters, as demonstrated through SEM images (Fig. 5) taken at a suspension pH of 7.6 ± 0.3.

3.1.3. Aggregation of Ag NP

For most treatments, the measured aggregation kinetics data was very well described by the first order model (Eq. (1); Figs. A.1., A.2., and A.3. in the appendix). In most cases, the coefficient of determination (R^2) was above 0.80 with the exception of the treatment containing 9 mmol/L Ca^{2+} and 10 mg/L Ag ($R^2 = 0.61$). This low value for R^2 may be explained by the highly scattered particle radii (data not shown), which is probably due to sedimentation overlaying the aggregation process observed by DLS. At every used Ca^{2+} concentration (i.e. at 1.5 and 9 mmol/L), the final particle diameter increases with increasing Ag NP concentration (Table 2). At Ag NP concentrations of 0.5 and 5 mg/L, particle diameters do not differ significantly between the two different Ca^{2+} concentrations (Table 2). However, at Ag NP concentrations of 10 mg/L the difference in Ca^{2+} concentration has an impact on the final particle diameter (Table 2). This suggests a combined effect of two parameters: The increasing nanoparticle concentration may result in an increasing collision efficiency. This collision efficiency may be further enhanced by the compressing effect of the diffusive double layer caused by the Ca^{2+} ion, which is higher at 9 mmol/L Ca than at 1.5 mmol/L Ca.

Aggregation of Ag NP in the soil solution follows a different trend than aggregation in the 1.5 mmol/L Ca^{2+} solution. While particle diameters in the Ca^{2+} solution increase with increasing Ag NP concentration (i.e. demonstrating that an increasing particle concentration leads to an increase in cluster size due to enhanced collision but irrespective of any additional steric or charge effects), this is only the case for Ag NP concentrations of 0.5 and 5 mg/L in the soil solution (Fig. 6, Table 2). At 10 mg/L Ag NP, particle diameters are smaller than at 5 mg/L Ag NP. This may be attributed to steric effects of organic matter, which only seem to come into play at higher Ag NP concentrations. At these higher Ag NP concentrations, NP collide more often with each other and the prevention of particle attachment by DOM thus becomes more effective, leading to the formation of smaller aggregates. At smaller Ag NP concentrations, the likelihood of particles colliding is lower. Thus, the steric protection induced by DOM does not play such a relevant role as at higher Ag NP concentrations.

Table 2
Modelled parameters d_∞ (particle diameter at $t = \infty$) and k (rate constant) of citrate-stabilized Ag NP aggregated in different solutions for 1 1/2 h. Fluctuations are given as standard deviations.

Ag NP conc. [mg/L]	Ca solution [1.5 mM Ca^{2+}]	Ca solution [9 mM Ca^{2+}]	Soil solution [1.5 mM Ca^{2+}]
	d_∞ [nm]		
0.5	187 ± 15	188 ± 35	168 ± 14
5	1051 ± 123	755 ± 191	1551 ± 946
10	1418 ± 217	2237 ± 451	1033 ± 259
	k [h^{-1}]		
0.5	2.8 ± 0.0	4.2 ± 1.0	2.4 ± 1.0
5	1.7 ± 0.5	3.2 ± 0.9	1.7 ± 1.2
10	2.3 ± 1.0	2.0 ± 0.3	2.3 ± 0.4

Secondary precipitates of AgCl are known to lead to bridging between individual Ag NPs (Li et al., 2010), thus contributing to aggregation. However, with a maximum concentration of 4 μg/L Ag (see chapter 3.2.) in solution and a chloride concentration of 10.2 mg/L these values fall below the solubility product of AgCl ($1.61 * 10^{-10}$ mol^2/L^2; D'Ans and Lax, 1967). Hence, the formation of AgCl may be ruled out.

3.2. Release of Ag^+ ions

Results showed that equilibration in both media (i.e. Millipore and soil solution) leads to a release in Ag^+ ions (Fig. 7), however, the soil solution suppresses Ag^+ release, presumably due to the adsorption of organic matter from the soil solution. This assumption is supported by Liu and Hurt (2010). The authors found natural organic matter (NOM; i.e. Suwannee River humic acid II and fulvic acid I standards; International Humic Substance Society) to block reactive sites on the particle surface. Similarly, Cornelis et al. (2012) also found a drastic decrease in the

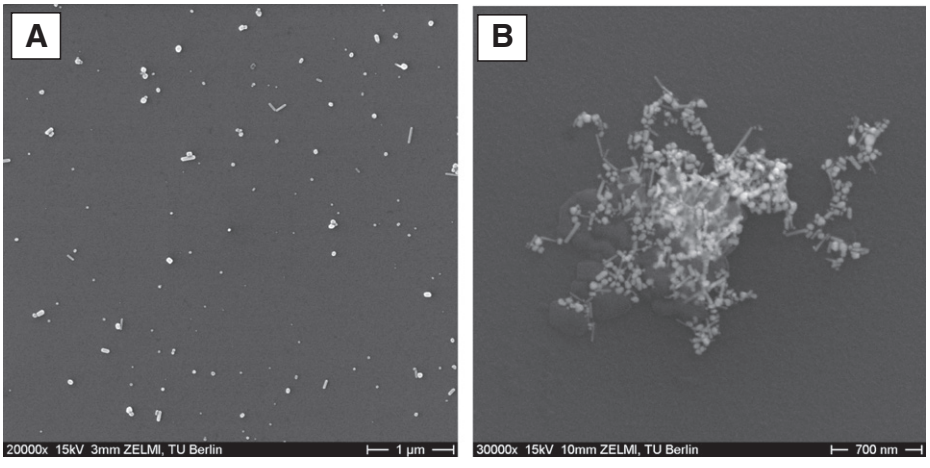

Fig. 5. Scanning electron microscopy image of citrate-stabilized Ag NP following equilibration in (A) Millipore water and (B) soil solution.

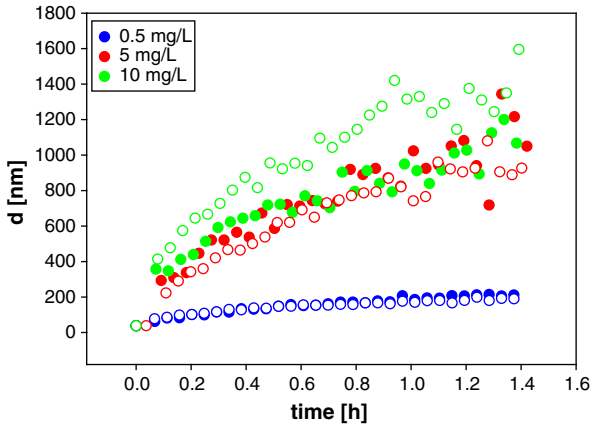

Fig. 6. Particle diameter of citrate-stabilized Ag NP equilibrated in 1.5 mmol/L Ca^{2+} solution (open symbols) and soil solution (closed symbol) with different initial Ag NP concentration as a function of time.

release of Ag^+ ions in an artificial soil solution containing Suwannee River fulvic acid in comparison to soil solution containing no organic matter. However, a more detailed comparison with this study is not possible as parameters such as Ag NP concentration, concentration and composition of organic matter as well as NP coating differ greatly from each other. According to Li et al. (2010) one may assume that Ca^{2+} would facilitate Ag oxidation by displacing Ag^+ ions from the NP surface. However, this effect does not seem obvious in our experiments or it might be overridden by the adsorption of DOM.

The additional release of Ag^+ ions after exchange with NH_4^+ demonstrates that additional Ag^+ ions were sorbed to Ag NP surface (Fig. 7). While in Millipore water this only occurs as a trend the observation is significant in soil solution. The concentration of dissolved Ag ions increases from 1 ± 0 to 4 ± 1 μg/L in soil solution and from 90 ± 13 to 211 ± 84 μg/L in Millipore water. This suggests a lower amount of exchangeable Ag^+ on the surface of soil-aged Ag NP than in Millipore water, which demonstrates that soil-aged Ag NP contains a lower amount of sorbed Ag^+ ions and supports the idea that DOM coatings may inhibit Ag^+ oxidation (see our own data above as well as Liu and Hurt, 2010). However, this also implies that even if soil solution inhibits Ag^+ release, soil-aged Ag NP may still act as a sink for Ag ions as Ag^+ ions sorbing on the particle surface may be released into solution.

3.3. Sorption of Ag NP onto silt grains

Zeta potential of bare Ag NP was −36 mV and of citrate-stabilized Ag NP −59 mV. Despite of this pronounced difference in zeta potential

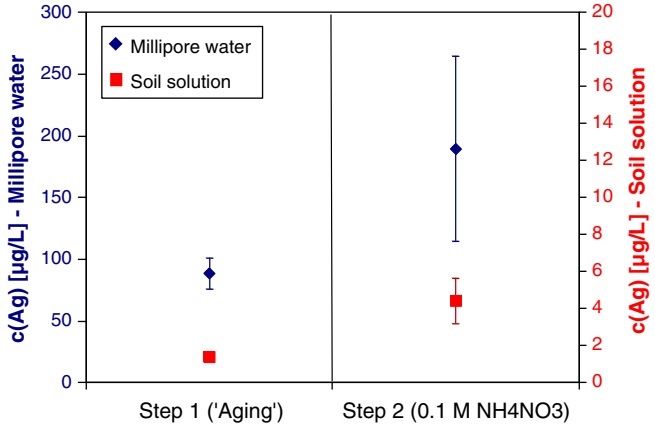

Fig. 7. Release of Ag ions from Ag NP following equilibration in Millipore water and soil solution for 24 h and subsequent equilibration in 0.1 M NH_4NO_3 solution.

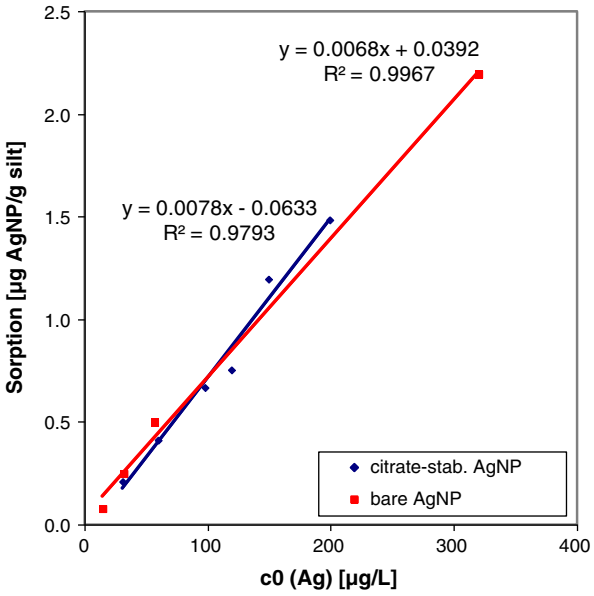

Fig. 8. Sorption of bare and citrate-stabilized Ag NP to silt grains as a function of initial Ag concentration.

sorption curves were very similar (Fig. 8), suggesting that the zeta potential is not the driving force which governs Ag NP sorption. Our observation that citrate-stabilized Ag NP and bare Ag NP show similar sorption is in contrast to the observation by Abraham (2015), who found a ten-fold lower sorption to SiO_2, glass and sand surfaces for citrate-stabilized Ag NP compared to bare Ag NP. Also, slopes for sorption isotherms in the dispersion are clearly higher for sorption of the same Ag NP to SiO_2, sand and glass surfaces (Abraham et al., 2013 for bare Ag NP and Abraham, 2015 for citrate-stabilized Ag NP) than in our study. A further reduction of attachment of Ag NP in the presence of dissolved NOM was observed in both mentioned studies (Abraham, 2015 for bare and citrate-stabilized Ag NP, and Thio et al., 2012 for citrate-stabilized Ag NP). The reduction in sorption was explained by a combination of increased colloidal stabilization of Ag NP in the dispersion and sorption of humic acid to the sorbent surfaces (Abraham, 2015). The comparably low sorption of Ag NP in our study compared to the studies of Abraham (2015) and Abraham et al. (2013) might thus also arise from low amounts of organic matter present in the silt (Abraham, 2015). The responsible mechanism of Ag NP attachment is still unclear and remains to be elucidated.

4. Conclusions

Our data show that Ag NPs undergo various processes with soil particles and with the soil solution. Sorption of Ag NP to silt particles is not governed by NP surface charge. Exposure of Ag NP to soil solution decreases the release of ionic Ag, presumably due to organic matter coatings. Bare Ag NPs sorb DOM from the soil solution, with short-chained DOM being preferentially adsorbed over long-chained, aromatic DOM. The sorption of solutes such as Ca^{2+} from soil solution decreases Ag NP stability, DOM has a concentration-dependent stabilizing effect. The stabilizing effect of DOM is relevant especially at high Ag NP concentration. Our results clearly demonstrate that Ag NP aggregation is strongly determined by Ag NP concentrations. Thus, caution should be taken when transferring results obtained from high nanoparticle concentrations in laboratory studies to lower, i.e. more environmentally relevant concentrations. In summary our results suggest that ageing in soils' environment decreases the ecological risk of Ag NPs.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.10.108.

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